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# Selectivity in Ligand Binding to Uranyl Compounds: A Synthetic, Structural, Thermodynamic and Computational Study

## Fuel Cycle Research and Development

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## Background and Significance

The uranyl cation ($UO_2^{2+}$) is the most abundant form of uranium on the planet. It is estimated that 4.5 billion tons of uranium in this form exist in sea water. The ability to bind and extract the uranyl cation from aqueous solution while separating it from other elements would provide a limitless source of nuclear fuel. A large body of research concerns the selective recognition and extraction of uranyl. A stable molecule, the cation has a linear O=U=O geometry. The short U-O bonds (1.78 Å) arise from the combination of uranium 5f/6d and oxygen 2p orbitals. Due to the oxygen moieties being multiply bonded, these sites were not thought to be basic enough for Lewis acidic coordination to be a viable approach to sequestration.

We believe that the goal of developing a practical system for uranium separation from seawater will not be attained without new insights into our existing fundamental knowledge of actinide chemistry. We posit that detailed studies of the kinetic and thermodynamic factors that influence interactions between f-elements and ligands with a range of donor atoms is essential to any major advance in this important area. The goal of this research is thus to broaden the coordination chemistry of the uranyl ion by studying new ligand systems via synthetic, structural, thermodynamic and computational methods. We anticipate that this fundamental science will find use beyond actinide separation technologies in areas such as nuclear waste remediation and nuclear materials.

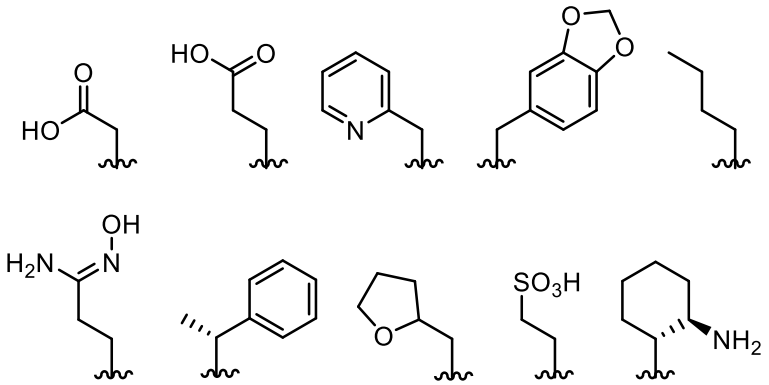
Most strategies toward uranyl sequestration involve ligands solely bonding to the uranium center equatorially in a planar geometry. Research has shown that when coordinating strong $\sigma$ and $\pi$ donating ligands to the equatorial plane, the added electron density softens the U(VI) center giving some Lewis basicity to the axial oxygen atoms as the U-O bond weakens. Several innovative ligand designs dually bond to both the equatorial plane and the axial oxo groups.

A ligand designed by Raymond and coworkers illustrates this approach by containing carboxylate groups as electron donors to the equatorial plane, while also containing a secondary amine to hydrogen bond with a uranyl oxygen. Such an approach is selective for the target species, as no other present cationic species would have the particular geometry of uranyl. Two reports have shown that the bonding of equatorial NCN ligands to uranyl weakens the U-O stretch frequency. This bond weakening coincides with increased Lewis basicity of the oxo ligands as illustrated by the addition $B(C_6F_5)_3$, yielding the complex $UO\{OB(C_6F_5)_3\}(NCN)_2$. This is the first example of an oxo ligand being functionalized by borane, albeit a highly Lewis acidic one. Additionally several studies report uranyl oxo ligands interacting with transition and alkali metal cations.

**Combinatorial peptoid ligands**

Recently, a new peptoid library containing some new side chains as well as ones used in the first- and second-generation libraries was synthesized. The new side chains contain some groups that are expected to bind to uranyl with a higher affinity (amidoxime) than just the carboxylates used previously.

Statistical analysis has been performed on the hits from the second library, and although there were a lot of sequences, two main observations are significant. First, the first residue (closest to the linker) appears to be statistically random, which is partially explained by sterics around the metal. It is unlikely that all four different groups can all fit equatorially around uranyl and so the outer three are favored for binding due to reduced sterics from the linker. This means that future libraries can either only contain three residues, or have only a limited selection of residues at the fourth position to alter sterics but not bind. This will allow us to screen more efficiently in the future. The other main observation is that longer carboxylates are still the dominant binding groups. Other donor groups that were not as strong were included such as the picolylamine, but future libraries will include other residues that are anticipated to bind with a higher affinity. The observations with chain length are also similar to past results, with the longer chains being favored which likely allows them to reach around and have multiple groups bind to the uranyl.




Side-chains included in third-generation combinatorial peptoid library. The five top row side-chains were found in previous uranyl-binding peptoids from previous screens.

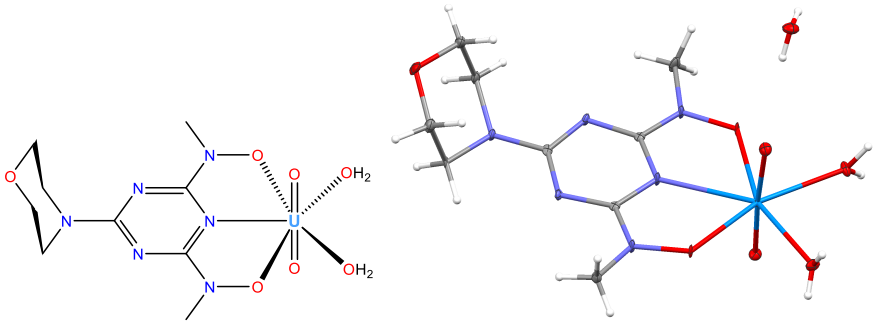
After screening this library, preliminary data shows that several of the new side chains are present in sequences along with carboxylates and others in previous libraries. Somewhat surprisingly, the non-binding submonomers are abundant in the first position although the full sequences will be more telling. A full scaled-up synthesis of the library is in progress and it will be screened in the same manner as before, although with optimized conditions.

**New ligand design and uranyl coordination (with Dr. Linfeng Rao, LBNL)**

Along with the set of known amidoxime and hydroxamic acid ligands, we have also been working on a triazine-hydroxylamine ligand in collaboration with Oak Ridge National Lab. Computational work has been performed on this ligand and it should be significantly more selective than amidoxime A for uranyl. We have performed potentiometric titrations to obtain binding constants for this system. While its affinity is lower, it is indeed more selective for uranyl over vanadium. A 1:1 complex is favored at pH 3-8, while a 2:1 complex is more stable at higher pH. The exact cause of this is unknown, and this is in contrast to amidoxime A which favors 2:1 binding at all pH values.

In addition to potentiometric studies, NMR experiments were also performed to confirm the solution binding modes. Although the studies were somewhat limited by solubility and broad peaks, we did observe the expected species and interactions. In addition to 1H NMR in water, we also did experiments in DMSO and methanol, and while they did not provide aqueous binding information, they are in agreement with reactivity trends seen across the solutions. 13C NMR was used to help assign signals.

In the course of these studies, we isolated the 1:1 complex which was used in some NMR experiments. This was also crystallized from water and the crystal structure was obtained. In the solid state, the chelating tridentate binding mode is favored, as expected. The overall binding is similar to amidoxime A. There are two water molecules also bound to the uranyl, and these appear to be strongly bound, as they are not replaced by other solvents. At high pH, this complex is soluble, which is proposed to be an anionic 1:1 species that is not in the speciation diagram. Further work and collaboration is in progress to fully understand this system and see how well it agrees with theory.




Structure of $H_2$Bihyat/uranyl

**Metal – amidoxime kinetic studies (with Dr. Linfeng Rao, LBNL)**

In order to see if kinetics can be exploited for selectivity even if thermodynamics does not favor selective uranium binding, stopped-flow kinetics was used to study relative kinetics of relevant metals. The uranyl system was studied in the presence of carbonate and calcium or other ions. These conditions are necessary for solubility and ligand stability, and the system is similar

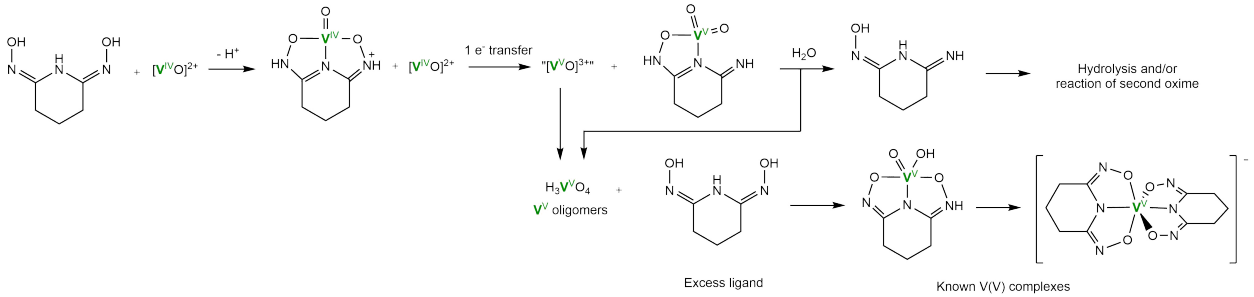
to seawater. Similar to the other metals, the complexation appears to be first order in ligand and first order in uranyl. However, two steps are seen in the absorbance graph, where the first is the formation of the 1:1 complex and the second is formation of the 2:1 complex. These two steps cannot be examined independently, however, both are much faster than the iron and especially vanadium complexation reactions. Carbonate and other metal ions play a significant role in the binding kinetics as well as thermodynamics; carbonate slows the reaction somewhat and also means that less complex is formed, and at high carbonate concentrations the two distinct steps are lost, and only one process is seen as the two reactions now occur on similar time scales.

Vanadium and iron were studied in a similar fashion, and vanadium was found to be significantly slower than uranium or iron in complexing amidoxime. This is consistent observations from marine tests, as uranium and iron reached equilibrium concentrations faster than vanadium. Recently we have written up this work and published it, concluding these studies.

**Redox chemistry of amidoxime-vanadium complexes**

Continuing our previous work with amidoxime A and vanadium(V), we are also interested in the chemistry of vanadium(IV). Vanadium is present in both oxidation states in the ocean with the majority (V). However, both need to be considered to fully understand U/V competition, especially if there is possible reactivity between the two oxidation states. Initially, amidoxime A was investigated with V(IV) due to its surprising reaction with V(V) to form a non-oxido complex. Several attempts were made to synthesize a stable V(IV) complex with different vanadium sources, pH, and other conditions, however, in water the reaction mixture invariably produced the V(V) ligand complex. This implies that whatever V(IV) species is being formed is unstable and quickly oxidizes to V(V). In water both oxidation states are typically stable so this is somewhat surprising.

After observing this reactivity, the redox chemistry of amidoximes was explored in more detail. More experiments were performed, both NMR as well as large-scale, and the reaction was found to result in the transfer of an oxygen atom from the ligand to vanadium. However, since the reduction is a one-electron process and the ligand reaction is two-electron, two equivalents of vanadium react with one oxime, or up to four with one ligand. As a result of this, the 4:1 stoichiometry results in excess ligand generally being present, leading to known V(V) complexes after oxidation is complete. The reaction is homogeneous and proceeds rapidly, reflecting the strongly chelating nature of the amidoxime. We propose the following reaction mechanism:



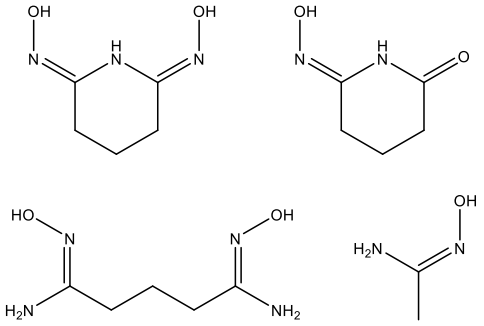

Mechanism of V(IV) – amidoxime reactivity

In addition to amidoxime A, the reactivity of V(IV) was examined with other oximes, namely amidoxime B and acetamidoxime, as well as an oxime, acetone oxime, to assess the generality of the reaction. In these cases, similar oxygen atom transfer is observed, however, the reaction requires vanadium dioxide to be produced as an intermediate. When small amounts of base are added, a $VO_2$ colloid is formed resulting in a grey color although it is not always visible as cloudiness. Due to the heterogeneous nature of the reaction, it proceeds relatively slowly, and we attribute the necessity of the heterogeneity to the fact that two electrons need to be transferred instead of one. Because these substrates are not strong ligands, two equivalents of vanadium would need to interact with one ligand at the same time, which is unlikely so the reaction would not proceed to a meaningful extent. The reaction with acetone oxime in particular is quite clean and demonstrates that O-atom transfer is indeed what is occurring.

This reactivity and lack of isolable V(IV) complex was confirmed using cyclic voltammetry techniques. The V(V) complexes proved to be very difficult to reduce and reductions were generally irreversible, demonstrating the lack of stability of the reduced species. This reaction means that V(IV) will damage polymer sorbents irreversibly, reducing capacity for uranium. While vanadium is mostly present as V(V) in the ocean, V(IV) still is non-negligible, accounting for 10-20% of total vanadium. This reaction or similar reactions of reduced metals can be a significant cause of observed degradation.

**Potentiometric and structural studies of amidoximes (with Dr. Linfeng Rao, LBNL)**

In order to understand selectivity of uranium over other metals, past work has been done to understand how amidoxime A binds to copper, iron, and vanadium. Stability constants have been determined for these metals, which has determined that although amidoxime A is good for uranium, its selectivity favors vanadium, and both copper and iron are seen in significant amounts in marine tests



Ligands used in potentiometric experiments

Although amidoxime A is the functional group that has been targeted the most in the past, other functional groups are present in significant amounts on polymer sorbents, the main ones being the other ligands shown here. We have performed potentiometric experiments with other metals and these ligands in order to assess the species formed and their stability. Work with acetamidoxime and vanadium had been performed previously, on a larger project in

collaboration with Oak Ridge National Lab. That work is in the process of being published, studying vanadium complexation to amidoximes in depth.

Acetamidoxime is representative of an isolated amidoxime group and is the simplest unit on sorbents that binds uranium. We tested this ligand with iron and copper, and iron was shown to not form meaningful complexes, as in all experiments iron hydroxide precipitated, indicating that any complexes that could form are too weak to prevent hydrolysis. On the other hand, copper did bind reasonably well, forming several 1:2 (M/L) complexes. Similar trends are observed with amidoxime B and C, where iron formed only weak complexes while both ligands are significantly better at binding copper. These observations are somewhat surprising, as significantly less copper is observed on polymers than the other metals discussed here. It is not as big an issue as vanadium though, as its removal generally does not damage the polymer irreversibly. Amidoxime C is generally not a good ligand, and its uranyl complex is significantly weaker than the other ligands as well, so it not binding to vanadium and only forming weak iron complexes is unsurprising.